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The Gaussian wave packet transform: Efficient computation of the semi-classical limit of the Schrödinger equation. Part 2. Multidimensional case

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ABSTRACT

A Gaussian wave packet transform is developed for the efficient computation of the semi-classical limit of the multidimensional Schrödinger equation with smooth potential. This transformation, based on Gaussian wave packets, yields a Schrödinger-type equation that is very amenable to numerical solution in the semi-classical limit. The transformed Schrödinger equation is solved with a 4th order splitting method. The wave function can be reconstructed from the transformed wave function whereas some expectation values can easily be evaluated directly. The number of grid points needed per degree of freedom is small enough that computations in dimension of up to 4 or 5 are feasible without the use of any basis thinning procedures.

1. Introduction

In this paper, we develop an efficient computational approach for the semi-classical limit of the Schrödinger equation in the case of many degrees of freedom. Our approach is based on an extension of the Gaussian Wave Packet Transform developed in Ref. [16] for the one dimensional case. This formulation transforms the Schrödinger equation into another partial differential equation which is much more amenable to computation in the semi-classical limit. This is a challenging problem that has many applications in chemistry (e.g. [17]).

To better understand the computational issues at hand, let us consider the scattering of a Carbon atom of 1 eV from some sort of scattering potential. Ideally we would like to bring the particle in from infinity, have it scatter, and follow it as it moves back out to infinity. Intermolecular forces have ranges on the order of several angstroms, therefore for this problem we would need to consider a computational domain that is at least 10 to 20 angstroms in size.

According to de Broglie, the wavelength of a particle with momentum P_0 is

$$\lambda = h/P_0,$$

where h is Planck's constant ($h = 6.626 \times 10^{-34}$ kg m^2/sec). Now for a free particle, $P_0 = \sqrt{2mE_0}$ where E_0 is its energy and m is its mass. Therefore

$$\lambda = h/\sqrt{2mE_0}.$$

The mass of Carbon is $m = 1.9985 \times 10^{-26}$ kg and if we take $E_0 = 1$ eV (1.60217×10^{-19} kg m^2/sec^2) then

$$\lambda = 8.24 \times 10^{-12} \text{ m} = 0.0824 \text{ Å}.$$

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If we wish to compute the scattering problem by directly solving the Schrödinger equation then we will need approximately 10 grid points per wavelength. Therefore for a problem like this on a domain the size of 10 Å one would need at least 10^3 grid points. This is quite manageable in one and two degree of freedom systems but for 3 or more it becomes prohibitively expensive.

Before we begin the discussion of the results of our paper it is useful to present the dimensionless form that will be used here.

1.1. Dimensionless form of the Schrödinger equation

We start with the Schrödinger equation with one degree of freedom:

$$i\hbar\Psi_\tau = -\frac{\hbar^2}{2m}\Psi_{XX} + \mathcal{U}(X)\Psi, \tag{1}$$

where Ψ is the wave function, $\hbar = h/2\pi$ is the reduced Planck's constant, m is the mass of the particle, and $\mathcal{U}(X)$ is the potential energy. We shall let Λ denote a length associated to the potential energy. For example, if $\mathcal{U}(X) = e^{-X/a}$ then $\Lambda = a$. If E_0 is the total energy then $\sqrt{2mE_0}$ is a momentum scale and $T = \Lambda\sqrt{m/(2E_0)}$ is a time scale. The momentum scale is combined with the de Broglie formula to produce a quantum length scale $\lambda = h/\sqrt{2mE_0}$.

Notice that the uncertainty principle tells us

$$\Delta X \Delta P \geqslant \hbar/2,$$

where ΔX and ΔP are the uncertainties in position and momentum respectively. One can nondimensionalize the above relationship by dividing both sides by $\sqrt{2mE_0}$ and Λ to obtain

$$\underbrace{\frac{\Delta X}{\Lambda}}_{\Delta x}\underbrace{\frac{\Delta P}{\sqrt{2mE_0}}}_{\Delta p} \geqslant \frac{\hbar}{2\Lambda\sqrt{2mE_0}} \equiv \varepsilon/2, \tag{2}$$

where Δx and Δp are the respective dimensionless uncertainties in position and momentum and

$$\varepsilon = \frac{\hbar}{\Lambda\sqrt{2E_0 m}}.$$

This is a dimensionless Planck's constant. Finally, in view of the definition of the quantum length scale, λ, ε can be written as

$$\varepsilon = \frac{\lambda}{2\pi\Lambda}.$$

A typical length scale for an intermolecular potential is about 2 Å. So for 1 eV Carbon atoms we have that $\varepsilon \approx 0.006$ which is small but not negligible.

The dimensionless Planck's constant defined above also naturally comes out of the Schrödinger equation. To see this we will rescale both space $X = Lx$ and time $\tau = Tt$. The condition

$$1 = \int_{\mathbb{R}^N} \left|\Psi(X,0)\right|^2 dX = \int_{\mathbb{R}^N} \left|\psi(x,0)\right|^2 dx$$

suggests to set

$$\Psi(X,\tau) = \psi(x,t)L^{N/2}.$$

Applying the change of variables to (1), and dividing by $2E_0L^{N/2}$, one obtains

$$\frac{i\hbar}{2TE_0}\psi_t = -\frac{\hbar^2}{4mL^2E_0}\psi_{xx} + \frac{\mathcal{U}(xL)}{2E_0}\psi. \tag{3}$$

Now we choose

$$T = \Lambda\sqrt{m/(2E_0)} \quad \text{and} \quad L = \Lambda,$$

and find

$$i\varepsilon\psi_t = -\frac{\varepsilon^2}{2}\psi_{xx} + V(x)\psi, \tag{4}$$

where $V(x) = \mathcal{U}(x\Lambda)/(2E_0)$. The dimensionless momentum operator is $\hat{p} = -i\varepsilon\partial_x$. This is the dimensionless form of the Schrödinger equation we shall use in this paper.